



# Article New Evidence of Submarine Exhalative Sedimentation in the Uranium-Polymetallic Phosphorite Deposit in Baizhuyu, Hunan, China

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**Abstract:** There are as many as 25 kinds of minerals (including non-ferrous metals, ferrous metals, rare and dispersed elements, precious metals, non-metallic and energy minerals) enriched in uranium-polymetallic fertile beds in black rock series, which is therefore widely attracting scholars all over the world. However, there is still great controversy in terms of the metallogenic mechanism in such beds. The black rock series have been systematically sampled from the Baizhuyu deposit in northwestern Hunan Province, China based on field geological and radioactivity surveys. Major and trace elements as well as rare earth elements (REE) of uranium-polymetallic phosphorite and its wall rocks were analyzed. Furthermore, carbon and oxygen isotopes, Sm-Nd isotopes, and mineralogy of the Baizhuyu deposit were studied. The results show that dolomite is a normal marine sediment, while and uranium-polymetallic elements were pre-enriched in phosphorites and black carbonaceous argillaceous shales and slates that formed from marine sedimentation and submarine exhalative sedimentation. Hydrothermal reworking to uranium-polymetallic phosphorites is significant as a result of submarine exhalative sedimentation. The research results of this paper can support a better understanding of metallogenesis and the future exploration of uranium-polymetallic phosphorite in the Lower Cambrian Niutitang Formation in the study area.

**Keywords:** geochemical characteristics; uranium-polymetallic phosphorite; submarine exhalative sedimentation; Baizhuyu deposit

# 1. Introduction

Black rock series, widely distributed worldwide, mainly formed on a global scale in semi-deep sea-deep sea, swamp, or stagnant coastal-shallow sea environments, and consist of dark gray-black siliceous rocks, carbonaceous rocks, argillaceous rocks (tuffs), and their metamorphosed rocks [1–4]. They occur in the Lesser Himalayas of India, Iran, northern Pakistan, southern France, Wales, England, the Netherlands, Germany, Russia, northern Oman, southern Australia, Canada, Mongolia, Central Asia, and China [5]. In China, the black rock series formed from the Proterozoic to Tertiary. They are mainly located in the eastern, western, and northern margins of the Yangtze terrain, and the southern and northern margins of the black rock series, are commonly found at the base of the Lower Cambrian. There are as many as 25 kinds of minerals (including non-ferrous metals, ferrous metals, rare and dispersed elements, precious metals, non-metallic and energy minerals), which have a close genetic and spatial relationship with the uranium-polymetallic fertile beds in the black rock series, and often formed in large-super large deposits [7–12].



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The Baizhuyu deposit is one of the few Ni-Mo polymetallic deposits that is being mined from the black rock series. Moreover, this kind of deposit, in which Ni and Mo coexist and both reach the economic mining conditions, is rare in the world [13–15]. The metallogenic mechanism of uranium-polymetallic phosphorite in the Lower Cambrian Niutitang Formation is still controversial. There are five main points of view. (1) Genesis of celestial impact, which is according to the unique element assemblage and Ir anomaly characteristics of the black rock series at the bottom of the Lower Cambrian in South China. Fan Delian proposed that platinum group elements (PGE), Co, and Ni might have been sourced from other places [16,17]. (2) Genesis of normal marine sediments, given that the Mo isotopic composition of the polymetallic rich beds of the black rock series is principally consistent with the values of modern seawater and the ore-forming age is consistent with the stratigraphic age of the Niutitang Formation, so it is speculated that the Ni-Mo polymetallic rich beds are normal marine sedimentary deposits [18–21]. (3) Genesis of submarine hydrothermal exhalation, because the extraordinary polymetallic enrichment in the black rock series has been found to be closely related to submarine exhalative sedimentation [13,22–26]. (4) Genesis of magmatic volcanic debris, which was raised by Luo Taiyi, who believes that alkaline-ultramafic magmatic activity exists during the Early Cambrian in the deep part of the Ni-Mo ore bed in the Songlin mining area of Zunyi, and the dominant material source is in deep magmatic rock. The metallogenic process experienced magmatism, hydrothermal sedimentation, and mechanical sedimentation, which is the product of the strong eruption period of deep magmatic activity [27,28]. (5) Biogenesis [29].

In this study, aiming at the systematic anatomy of the Baizhuyu uranium-polymetallic deposit in northwestern Hunan, on the basis of geological and radiological investigations of the black rock series in South China, samples collected from tunnel sections in the Baizhuyu deposit were analyzed for major elements, trace elements, and rare earth elements as well as carbon and oxygen isotopes and Sm-Nd isotopes, and were also studied through the Advanced Mineral Identification and Characterization System (AMICS), an automatic mineral parameter quantitative analysis tool. We aimed to place a better understanding on: (1) the elemental geochemical characteristics of the uranium-polymetallic fertile beds and its upper and lower host rocks; (2) the mineralogical characteristics of the uranium-polymetallic phosphorite; and (3) the enrichment mechanism of the uranium-polymetallic phosphorite.

#### 2. Geological Characteristics of the Baizhuyu Deposit

Figure 1 illustrates the uranium-polymetallic phosphorite deposit in Baizhuyu. The stratigraphic structure is relatively stable regionally. The Lower Cambrian Niutitang Formation uranium-polymetallic phosphorite is the main ore-bearing bed of the Baizhuyu deposit. It is exposed along two wings of Cili depression. It has a clear boundary with the underlying gray-white massive dolomite of the Sinian Dengying Formation and the overlying black carbonaceous argillaceous shale and slate of the Lower Cambrian Niutitang Formation. Occurrence, morphology, distribution, and scale of the uranium-polymetallic phosphorite layers were controlled by wavy landform of the ancient denudation surface of the Dengying Formation. The thickness of the uranium-polymetallic phosphorite layer varied (20~40 cm) in the Cili depression area. Additionally, uranium-bearing phosphorites could be observed at the bottom. The layer of black carbonaceous-argillaceous shales and slates of the Niutitang Formation was above the uranium-polymetallic phosphorite layer. The lithological conditions and stratigraphic contact relation are shown in Figure 2.



Figure 1. A schematic of the lithologic profile and sampling of the Baizhuyu deposit [30].



**Figure 2.** The lithological conditions of the uranium-polymetallic phosphorite layer and its contact with the upper and lower country rocks: (a) Contact of the Dengying–Niutitang Formations; (b) grey-white, thick, massive dolomite of the Dengying Formation (the arrowed points); (c) uranium-polymetallic phosphorite layer (the arrowed points); (d) black carbonaceous-argillaceous shales and slates (the arrowed points).

## 3. Materials and Methods

Thorough sampling of the uranium-polymetallic phosphorite layer in the Baizhuyu deposit was conducted. Four samples were taken every 10 cm. Meanwhile, two samples from the underlying dolomites and four samples from the overlying black shales were collected. Figure 2 shows the detailed sampling sites and sample numbers.

All of the studied samples were crushed and pulverized to 200 meshes before being analyzed. The major, trace, and rare earth elements of all samples, the C, O isotopes, and Sm-Nd isotopes of the uranium polymetallic phosphorite samples were analyzed. All analyses mentioned were completed at the Beijing Research Institute of Uranium Geology (BRIUG).

The major elements of the samples were determined by X-ray fluorescence spectrometer (XRF, PW2404 by Phillips) at a relative humidity of 33% and temperature of 23 °C. The trace and rare earth elements of samples were determined by inductively coupled plasma mass spectrometer (ICP-MS, ELEMENT XR) at a relative humidity of 30% and temperature of 20 °C. C and O isotopes of the samples were determined by mass spectrometer (MAT 253). PDB was employed as the standard for  $\delta^{13}$ C, while PDB and SMOW were employed as the standards for  $\delta^{18}$ O. The Sm-Nd isotopes of the samples were determined by a thermal surface ionization mass spectrometer (TIMS, ISOPROBE-T, by GV UK), at a relative humidity of 30% and temperature of 20 °C. The error was down to 2 $\sigma$ .

The mineral composition and characteristics were studied through the automatic quantitative analysis of mineral parameters at the Analytical Laboratory of BRIUG. The automatic mineral parameter quantitative analysis system consisted of a ZESS sigma300 high resolution field emission scanning electron microscope, BrukerXflash6130 X-ray spectrometer, and automatic mineral analysis data processing software. The test conditions were high vacuum mode, working voltage 20 KV, working distance 9.5–10 mm, aperture 120 µm.

#### 4. Results

#### 4.1. Geochemical Results of Major Elements

The major elemental composition of the dolomite, uranium-polymetallic phosphorite and black carbonaceous-argillaceous shales and slates are listed in Table 1. Dolomites were mainly composed of CaO and MgO, of which the average contents were 29.59% and 20.09%, respectively; the average content of SiO<sub>2</sub> was 3.13%; and the average content of loss on ignition (LOI) was 44.28%. The uranium-polymetallic phosphorites were mainly composed of CaO and P<sub>2</sub>O<sub>5</sub>, of which the average contents were 38.4% and 30.6%, respectively; the average content of SiO<sub>2</sub> was 9.56%; and the average content of LOI was 10.06%. Black carbonaceous-argillaceous shales and slates are mainly composed of SiO<sub>2</sub>, of which the average content was 61.89%; the average contents of Al<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O were 12.99% and 4.13%, respectively; and the average content of LOI was 13.78%. From the bottom (i.e., dolomite) to the top (i.e., shales and slates), the contents of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, and Fe<sub>2</sub>O<sub>3</sub> increased, the content of CaO in the overlying black carbonaceous-argillaceous shales and slates decreased drastically, and P<sub>2</sub>O<sub>5</sub> was significantly enriched in the uranium-polymetallic phosphorite layer of the Lower Cambrian Niutitang Formation.

#### 4.2. Geochemical Results of Trace Elements

The trace elements (U, Ni, and Mo) were enriched in the dolomites, uranium-polymetallic phosphorites, and black carbonaceous-argillaceous shales and slates when compared with the upper crust. Herein, uranium-polymetallic phosphorites exhibited the maximum enrichment coefficients. The grades of U, Ni, and Mo reached their minable industrial index of China and compared with the upper crust, the average enrichment coefficients of U, Ni, and Mo in the uranium-polymetallic phosphorites were 482.1, 341.1, and 1402.5, respectively [31]. Re, Tl, and V reached the Chinese minable industrial index as byproducts of the uranium deposit and the average enrichment coefficients of Re, Tl and V in the uranium-polymetallic phosphorites were 2.7, 40.0, and 14.6, respectively [32]. Figure 3 shows the primitive mantle standardized cobweb map of averages of some trace elements in dolomites, uranium-polymetallic phosphorites, and carbonaceous-argillaceous shales

and slates. As observed, these samples exhibited similar primitive mantle standardized distribution curves, while the enrichment coefficients of Ba, U, La, P, Sm and Y in the uranium-polymetallic phosphorites were higher than those in the other two kinds of ores.

Sample No.	BJY-9	BJY-8	BJY-7	BJY-6	BJY-5	BJY-4	BJY-3	BJY-2	BJY-1	BJY-0
Lithology	Black Carbonaceous-Argillaceous Shales and Slates				Uranium-Polymetallic Phosphorites				Dolomites	
SiO <sub>2</sub>	68.45	62.29	59.4	57.41	11.04	9.82	7.81	8.88	3.54	2.72
$Al_2O_3$	12.5	13.77	13.24	12.43	2.01	1.86	1.54	1.43	1.16	0.774
Fe <sub>2</sub> O <sub>3</sub>	3.18	1.69	2.47	2.76	1.68	1.84	1.43	1.5	0.84	0.419
MgO	1.54	1.63	1.6	1.4	0.512	0.522	0.449	0.513	19.94	20.23
CaO	0.22	1.12	2.43	3.29	39.72	36.94	38.53	37.42	29.27	29.9
Na <sub>2</sub> O	0.39	0.191	0.147	0.076	0.34	0.32	0.264	0.226	0.065	0.09
K <sub>2</sub> O	3.86	4.46	4.23	3.97	0.362	0.347	0.325	0.351	0.261	0.152
MnO	0.006	0.007	0.007	0.007	< 0.004	< 0.004	< 0.004	0.004	0.019	0.016
TiO <sub>2</sub>	0.517	0.622	0.604	0.585	0.082	0.07	0.062	0.073	0.061	0.03
$P_2O_5$	0.05	0.07	0.06	0.14	30.05	29.94	31.81	30.23	0.95	0.71
LOI	9.06	13.85	15.81	16.4	11.71	9.78	8.68	9.28	43.79	44.77
FeO	0.51	0.88	0.81	0.72	0.79	0.71	0.61	0.79	0.38	0.36
$\sum$	99.78	99.7	99.99	98.46	97.51	91.44	90.9	89.91	99.9	99.81

**Table 1.** The major elements of the samples from the Baizhuyu deposit ( $w_B/\%$ ).



Figure 3. The standardized cobweb map of the trace elements in the primitive mantle.

The content of Ba tends to be extremely low in modern seawater, but relatively high in submarine hydrothermal fluids. Hence, Ba is a key indicator element of hydrothermal sedimentation [33,34]. In hydrothermal sedimentation environments, uranium tends to be enriched due to accelerated sedimentation [35,36]. In the dolomites, as shown in Table 2, the contents of Ba were  $71.2 \times 10^{-6} \sim 122 \times 10^{-6}$  (average =  $96.6 \times 10^{-6}$ , average enrichment-deficit coefficient with the upper crust = 0.18), the Sr/Ba ratios were

0.79~1.92 (average = 1.36), and the U/Th ratios were 3.48~4.88 (average = 4.18). In uraniumpolymetallic phosphorites, the contents of Ba were  $6167 \times 10^{-6} \times 8424 \times 10^{-6}$ (average = 7471.5 × 10<sup>-6</sup>, average enrichment-deficit coefficient with the upper crust = 13.58), the Sr/Ba ratios were 0.06~0.08 (average = 0.07), and the U/Th ratios were 653.11~1083.78 (average = 821.48). In black carbonaceous-argillaceous shales and slates, the contents of Ba were  $1057 \times 10^{-6} \times 2267 \times 10^{-6}$  (average =  $1631.3 \times 10^{-6}$ , average enrichment-deficit coefficient with the upper crust = 2.97), the Sr/Ba ratios were 0.01~0.04 (average = 0.03), and the U/Th ratios were 3.3~3.98 (average = 3.65).

**Table 2.** The analytical results of the trace elements and rare earth elements in the Baizhuyu deposit  $(w_B/10^{-6})$ .

Sample No.	BJY-9	BJY-8	BJY-7	BJY-6	BJY-5	BJY-4	BJY-3	BJY-2	BJY-1	BJY-0
Lithology	Black Carbonaceous-Argillaceous Shales and Slates			Uranium-Polymetallic Phosphorites				Dolomites		
U	28.2	28.1	23.3	26.8	1156	1403	1604	1236	3.83	3.1
Ni	73.4	59.3	63	92.3	4769	8233	6711	7575	44.2	38.3
Мо	164	184	147	179	1844	2624	1981	1966	40.2	29.8
V	987	1241	915	894	832	1011	722	929	49	37.5
Re	0.156	0.193	0.123	0.121	0.996	1.39	0.798	1	0.007	0.009
Tl	2.42	7.63	9.82	9.81	21.7	39.8	26.2	32.2	0.205	0.097
Cu	53.1	46.9	50.2	59.4	244	348	309	319	31.2	9.81
Co	7.12	1.63	3.46	4.95	20.2	34.3	30.5	31.6	2.28	1.42
Zn	215	50.5	74.7	82.6	410	619	752	750	95.4	80
Cr	95.9	103	101	84.6	48.9	58.3	61.1	56	10.1	5.7
Rb	115	136	124	118	11.7	12.4	11.2	11	7.26	4.67
Κ	32,043	37,023	35,114	32,956	3005	2880	2697	2913	2166	1261
Ba	1904	2267	1057	1297	7988	7307	8424	6167	122	71.2
Th	8.15	7.26	7.06	6.74	1.77	1.95	1.48	1.49	1.1	0.635
Nb	10.3	12.7	11.6	10.7	1.56	1.45	1.06	0.932	1.86	0.639
La	29.9	33.3	31.8	31.9	125	147	151	142	6.34	4.33
Ce	52	53.9	53.3	53.9	102	121	121	110	7.04	4.17
Sr	21.6	35.9	35.7	51.5	462	531	523	480	95.9	137
Nd	25.6	22.5	23.2	23.5	99.2	122	120	111	7.39	4.2
Р	222	301	240	589	131,156	130,676	138,837	131,941	4163	3103
Zr	130	145	141	136	24.1	15.9	12.8	28.9	16.2	12.5
Hf	3.58	3.97	3.78	3.82	0.515	0.458	0.201	0.193	0.319	0.239
Sm	4.93	3.34	3.61	3.65	18.7	23.1	22.6	20.9	1.56	0.905
Ti	3099	3728	3620	3507	491	419	371	437	365	179
Y	45.9	25.8	27.1	27.5	373	451	469	410	19.6	12.1
Yb	4.3	2.9	3.03	3.19	13.2	16	17.8	15.2	0.951	0.653
Lu	0.558	0.415	0.403	0.415	1.52	1.9	2.11	1.62	0.189	0.095
δU	1.82	1.84	1.82	1.85	2	2	2	2	1.83	1.87
U/Th	3.46	3.87	3.3	3.98	653.11	719.49	1083.78	829.53	3.48	4.88
Sr/Ba	0.01	0.02	0.03	0.04	0.06	0.07	0.06	0.08	0.79	1.92
$\Sigma REE$	143.54	133.4	133.41	135.36	470.39	567.48	572.56	522.25	31.18	18.96
L∑REE	119.89	119.92	118.75	120	372.6	446.98	448.27	415.28	24.26	14.72
H∑REE	23.65	13.48	14.66	15.36	97.79	120.5	124.29	106.97	6.92	4.25
LREE/HREE	5.07	8.89	8.1	7.81	3.81	3.71	3.61	3.88	3.5	3.47
La/Yb	6.95	11.48	10.5	10	9.47	9.19	8.48	9.34	6.67	6.63
Ce/La	1.74	1.62	1.68	1.69	0.82	0.82	0.8	0.77	1.11	0.96
δCe	0.89	0.88	0.9	0.89	0.46	0.46	0.45	0.44	0.52	0.5
δEu	0.95	0.87	0.87	0.85	1.26	1.26	1.24	1.29	0.91	0.88

 $\delta U = 2U/(U + Th/3)$  (Wignall, 1994).

Abnormal enrichments of V, Cu, Zn, and Ba, which are indicator elements of hydrothermal fluids [37–39], were also frequently observed. The average enrichment-deficit coefficients of V in dolomites, uranium-polymetallic phosphorites, and black carbonaceousargillaceous shales and slates with the upper crust were 0.72, 14.56, and 16.82, respectively. The average enrichment-deficit coefficients of Cu in dolomites, uranium-polymetallic phosphorites, and black carbonaceous-argillaceous shales and slates with the upper crust were 0.82, 12.2, and 2.10, respectively. The average enrichment-deficit coefficients of Zn in dolomites, uranium-polymetallic phosphorites, and black carbonaceous-argillaceous shales and slates with the upper crust were 1.24, 8.91, and 1.49, respectively. The average enrichment-deficit coefficients of Ba in dolomites, uranium-polymetallic phosphorites, and black carbonaceous-argillaceous shales and slates compared with the upper crust were 0.18, 13.58, and 2.97, respectively.

## 4.3. Geochemical Results of REE

As shown in Figure 4b, normalized by North American shale composites (NASC), the REE distribution curves of the dolomites, uranium-polymetallic phosphorites, and carbonaceous-argillaceous shales and slates in the Baizhuyu deposit were horizontal or slightly inclined to the left. The overall average contents of REE in the dolomites, carbonaceous-argillaceous shales and slates, and uranium-polymetallic phosphorites were 25.07 ppm, 133.36 ppm, and 533.17 ppm, respectively.



**Figure 4.** (a) A schematic of w (La)/w (Yb)-w ( $\sum$ REE) in the Baizhuyu deposit; (b) the average NASC—normalized distribution curves of REE in samples collected from the Baizhuyu deposit.

For the dolomites,  $\delta Ce \text{ was } 0.5 \sim 0.52$  (average = 0.51) and  $\delta Eu \text{ was } 0.88 \sim 0.91$  (average = 0.90). For the uranium-polymetallic phosphorites, the  $\delta Ce \text{ was } 0.44 \sim 0.46$  (average = 0.45) and the  $\delta Eu \text{ was } 1.24 \sim 1.29$  (average = 1.26). For carbonaceous-argillaceous shales and slates, the  $\delta Ce \text{ was } 0.88 \sim 0.90$  (average = 0.89) and the  $\delta Eu \text{ was } 0.85 \sim 0.95$  (average = 0.89).

Figure 4a illustrates the w (La)/w (Yb)-w ( $\sum$ REE) of samples collected from the Baizhuyu deposit. As observed, uranium-polymetallic phosphorite samples were located in the intersecting area of alkaline rocks and granites; black carbonaceous-argillaceous shales and slates samples were located in the intersecting area of alkaline and sedimentary rocks (one sample) and the area of sedimentary rocks (three samples, near the areas of alkaline rocks and granites); the dolomite samples were located in the area of sedimentary rocks.

# 4.4. Results of C, O Isotopic Analysis

Compositions of light C, O isotopes can provide information about the fluid provenance [40]. Table 3 shows the C, O isotopic data of the uranium-polymetallic phosphorite samples.

SN.	Sample No.	Lithology	$\delta^{13}C_{V-PDB}$	$\delta^{18}O_{V\text{-}PDB}$	$\delta^{18}O_{V-SMOW}$
1	BJY-5		-3.4	-13.5	17
2	BJY-4	uranium-	-3.8	-14	16.5
3	BJY-3	polymetallic	-3.7	-13.6	16.9
4	BJY-2	phosphorite	-3.5	-12.1	18.4
Av	verage		-3.6	-13.3	17.2

**Table 3.** The C, O isotopic characteristics of the uranium-polymetallic phosphorite samples collected from the Baizhuyu deposit ( $w_B/\infty$ ).

The  $\delta^{13}C_{PDB}$  of marine sedimentary carbonates in crust is usually 0‰ and remain unchanged during the diagenetic process [41,42]; the  $\delta^{13}C_{PDB}$  of mantle-originated igneous rocks is usually -5% [40]; the  $\delta^{13}C_{PDB}$  of granites in South China is usually  $-37.9\sim-7.5\%$  [43]. The  $\delta^{18}O$  of detrital sedimentary rocks is usually aligned with that of the original rocks. However, the overall  $\delta^{18}O_{SMOW}$  of detrital sedimentary rocks is between that of unaltered volcanic rocks (5~15‰) and that of clay minerals (20~30‰) due to weathering and the components of clay minerals. The  $\delta^{18}O_{SMOW}$  of shales and submarine sediments is typically 5~25‰, while the  $\delta^{18}O_{SMOW}$  of modern marine limestones is typically 28~30‰ [44].

The  $\delta^{13}C_{V-PDB}$  of the uranium-polymetallic phosphorite samples was  $-3.4 \sim -3.8\%$ , with an average of -3.6%; the  $\delta^{18}O_{V-SMOW}$  of uranium-polymetallic phosphorite samples was 16.5~18.4‰, with an average of 17.2‰. The  $\delta^{13}C_{V-PDB}$  of the uranium-polymetallic phosphorite samples was between that of the marine sedimentary carbonates in the crust and mantle-originated igneous rocks and close to that of the mantle-originated igneous rocks. The  $\delta^{18}O_{V-SMOW}$  of the uranium-polymetallic phosphorite samples was between that of the shales and that of the submarine sediments. The C, O isotopes indicate hydrothermal reworking during conventional sedimentations.

### 4.5. Results of Sm-Nd Isotopic Analysis

Table 4 lists the Sm-Nd isotopic composition of the uranium-polymetallic phosphorite samples. Indeed, Nd isotopes can effectively reflect the provenance components and characteristics of sediments. McLennan et al. [45] claimed that the  $\varepsilon$ Nd of sediments originated from the ancient upper crust are usually below -10, while the  $\varepsilon$ Nd of sediments (rocks) originated from mid-ocean ridge basalt (MORB) are usually above +5. The  $\varepsilon$ Nd (0) of the uranium-polymetallic phosphorites in the Baizhuyu deposit was  $-21.26 \sim -16.03$  (see Table 4).

SN.	Sample No.	Lithology	Sm [×10 <sup>-6</sup> ]	Nd [×10 <sup>-6</sup> ]	<sup>147</sup> Sm/ <sup>144</sup> Nd	<sup>143</sup> Nd/ <sup>144</sup> Nd	εNd (0)
1	BJY-5	uranium- polymetallic phosphorite	18.1	96.9	0.113	0.511816	-16.03
2	BJY-4		21.8	117	0.1131	0.511792	-16.5
3	BJY-3		22.2	119	0.1122	0.511773	-16.87
4	BJY-2		20.1	110	0.1106	0.511548	-21.26

Table 4. The Sm-Nd isotopic composition of the samples from the Baizhuyu deposit.

 $(^{143}Nd/^{144}Nd)$  CHUR = 0.512638,  $(^{147}Sm/^{144}Nd)$  CHUR = 0.1967.

# 4.6. Results of Mineralogical Analysis

Based on the microscopic observation of the uranium-polymetallic phosphorites samples, further mineralogical analysis was undertaken using the Advanced Mineral Identification and Characterization System (AMICS). The results showed that the phosphorite was mainly composed of apatite and quartz, both of which account for about 90% weight percentage, therein, the apatite was 81.138% and the quartz 8.586%. Second, it also contained molybdenite, anhydrite, illite, pentlandite, pyrite, barite, uraninite, sphalerite, kaolinite, and rutile. The weight percentages were 3.429%, 1.478%, 1.426%, 1.352%, 1.027%, 0.533%, 0.355%, 0.011%, 0.005%, 0.002%, and 0.001%, respectively. Uraninite, molybdenite, pent-



landite, pyrite, and anhydrite were mainly distributed along the fractures. Molybdenum mainly exists in molybdenite, and nickel mainly exists in pyrite. For the space occupation of some of the major minerals, see Figure 5.

**Figure 5.** The backscattering image of the uranium-polymetallic phosphorite. Ap—Apatite; Pn— Pentlandite; Py—Pyrite; Mo—Molybdenite; Anh—Anhydrite; Qtz—Quartz; Ur—Uraninite; Brt— Barite. (a) Spatial relationship of minerals; (b) pitchblende, gypsum and pyrite distributed along fractures; (c) strawberry pyrite; (d) Mass distribution of nickel pyrite and molybdenite.

# 5. Discussion

Investigations of the geochemical characteristics of trace elements in the dolomite, uranium-polymetallic phosphorite, and black carbonaceous-argillaceous shales and slates from the Baizhuyu Deposit indicate that these samples had similar primitive mantle standardized distribution curves, suggesting similar provenances. Additionally, V, Cu, Zn, and Ba, which are indicator elements of hydrothermal fluids, were abnormally enriched in the samples of the uranium-polymetallic phosphorite and black carbonaceous-argillaceous shales and slates [37-39]. The enrichment-deficit coefficients of V, Cu, Zn, and Ba in the uranium-polymetallic phosphorite samples with the upper crust were 14.56, 12.2, 8.91, and 13.58, respectively. The enrichment-deficit coefficients of V, Cu, Zn, and Ba in the samples of black carbonaceous-argillaceous shales and slates with the upper crust were 16.82, 2.10, 1.49, and 2.97, respectively. The enrichment-deficit coefficients of V, Cu, Zn, and Ba in the dolomite samples with the upper crust were 16.82, 2.10, 1.49, and 2.97, respectively. The enrichment-deficit coefficients of V, Cu, Zn, and Ba in the Samples with the upper crust were 16.82, 2.10, 1.49, and 2.97, respectively. The enrichment-deficit coefficients of V, Cu, Zn, and Ba in the Samples with the upper crust were 16.82, 2.10, 1.49, and 2.97, respectively. The enrichment-deficit coefficients of V, Cu, Zn, and Ba in the Samples with the upper crust were 16.82, 2.10, 1.49, and 2.97, respectively. The enrichment-deficit coefficients of V, Cu, Zn, and Ba in the Samples with the upper crust were -0.72, -0.82, 1.24, and -0.18, respectively. The Sr/Ba ratio has also been widely used for the determination of rock provenance [34].

Previous studies have demonstrated that rock provenances of hydrothermal fluids and sedimentation are characterized by Sr/Ba ratio < l and Sr/Ba ratio > 1, respectively. The average Sr/Ba ratios of the samples of dolomite, uranium-polymetallic phosphorite, and black carbonaceous-argillaceous shales and slates were 1.36, 0.07, and 0.03, respectively. Likewise, geochemical characteristics of the trace elements demonstrate that hydrothermal fluids were present in the formations of uranium-polymetallic phosphorites and black carbonaceous-argillaceous shales and slates in the Baizhuyu deposit, but not in that of the dolomites in the Baizhuyu deposit.

Some studies have concluded that normal seawater sedimentations are characterized by the enrichment of light REE, resulting in right-inclined curves and abnormally positive Ce. The hydrothermal sedimentation curves are horizontal or slightly inclined, the light/heavy REE ratio is small, and Ce is abnormally negative [46]. Indeed, the  $\Sigma REE$ of normal seawater tends to be extremely low and REE-enriched sediments can barely be observed. Hence, high contents of REE in sediments are indicators of hydrothermal sedimentations. Some scholars have claimed that abnormally positive Eu is an indicator that highly reductive hydrothermal fluids are injected or that ocean basalts inherit the characteristics of the origin after submarine alteration [46-48]. This proposal has been widely supported. For instance, Michard et al. [49] reported that hydrothermal fluids in hydrothermal vents in the East Pacific Ocean and metallic sediments in the Galapagos Rift and the Red Sea hot brine pool had significantly abnormal positive Eu. The standardized distribution curves of REE in the NASC in the samples of dolomite, uranium-polymetallic phosphorite, and black carbonaceous-argillaceous shales and slates were horizontal or slightly inclined to the left and Ce was abnormally negative. The content of REE was minimized in dolomites, with an overall average of 25.07 ppm, and the average  $\delta$ Eu of 0.90. The content of REE was maximized in the uranium-polymetallic phosphorites, with an overall average of 533.17 ppm, and the average  $\delta Eu$  of 1.26. The overall average content of REE in carbonaceous-argillaceous shales and slates was 133.36 ppm and the average  $\delta$ Eu was 0.89. According to w (La)/w (Yb)-w ( $\sum$ REE), the uranium-polymetallic phosphorite and black carbonaceous-argillaceous shales and slates were located in the intersecting area of alkaline and sedimentary rocks or near the areas of alkaline rocks and granites. The characteristics of REE indicate the presence of hydrothermal reworking during the formation of uranium-polymetallic phosphorites and black carbonaceous-argillaceous shales and slates, especially uranium-polymetallic phosphorites. Additionally, hydrothermal modification is absent in the formation of dolomites.

The average  $\delta^{13}C_{V-PDB}$  of the uranium-polymetallic phosphorite samples was -3.6%, while that of the marine sedimentary carbonates in the crust and mantle-originated igneous rocks were 0% and -5%, respectively. The average  $\delta^{18}O_{V-SMOW}$  of the uranium-polymetallic phosphorite samples was 17.2%, which was within the range of those of the shales and submarine sediments ( $5\sim25\%$ ). The  $\epsilon$ Nd (0) was  $-21.26\sim-16.03$ , indicating that uranium-polymetallic phosphorites originated from the ancient upper crust and indirectly demonstrated the presence of hydrothermal modifications during the formation of uranium-polymetallic phosphorites.

The results of the microscopic observation and automatic quantitative analysis of mineral parameters showed that the uranium polymetallic phosphorite was mainly composed of apatite and quartz. Uraninite, molybdenite, pentlandite, pyrite, and anhydrite were mainly distributed along the fractures. There also existed molybdenite and pentlandite, barite, and rutile, which are typical hydrothermal minerals, indicating that hydrothermal alteration occurred on the basis of the marine sediments.

#### 6. Conclusions

(1) The dolomites in the Sinian Dengying Formation of the Baizhuyu deposit are mainly composed of CaO and MgO. The uranium-polymetallic phosphorites are mainly composed of CaO and P<sub>2</sub>O<sub>5</sub>,. The black carbonaceous argillaceous shales and slates had the highest SiO<sub>2</sub> content, followed by Al<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O, and the uranium-polymetallic phosphorite

belonged to the transitional type. From bottom to top, the contents of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, and Fe<sub>2</sub>O<sub>3</sub> increased, the contents of CaO in the overlying black carbonaceous-argillaceous shales and slates decreased drastically, and P<sub>2</sub>O<sub>5</sub> was significantly enriched in the uranium-polymetallic phosphorite layer at the bottom of the Lower Cambrian Niutitang Formation.

(2) Based on the field geological and radioactivity surveys, a comprehensive analysis of the major elements, trace elements, and REE of the samples of dolomite, uranium-polymetallic phosphorite and black carbonaceous-argillaceous shales and slates as well as the C, O isotopes, Sm-Nd isotopes, and mineralogical characteristics of uranium-polymetallic phosphorite demonstrate that the provenance of dolomites is marine sedimentation, while the provenances of uranium-polymetallic phosphorites and black carbonaceous-argillaceous shales and slates are marine sedimentation. Uranium-polymetallic pre-enrichment occurred during the formation of phosphorite and carbonaceous shales and slates. Meanwhile, hydrothermal reworking is evident in the uranium-polymetallic phosphorites, indicating the presence of submarine exhalative sedimentation during the formation of uranium-polymetallic phosphorites in the Baizhuyu deposit.

The research results of this paper can support a better understanding of the metallogenic theory and regularity on the unique uranium-polymetallic phosphorite in the Lower Cambrian Niutitang Formation in China, and will assist in the uranium exploration in the study area.

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